



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :  C23C 22/10		A1	(11) International Publication Number: <b>WO 96/19595</b>  (43) International Publication Date: 27 June 1996 (27.06.96)
<p>(21) International Application Number: PCT/US95/16231</p> <p>(22) International Filing Date: 22 December 1995 (22.12.95)</p> <p>(30) Priority Data: 6/320545 22 December 1994 (22.12.94) JP</p> <p>(71) Applicant (<i>for all designated States except US</i>): HENKEL CORPORATION [US/US]; Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (<i>for US only</i>): IINO, Yasuo [JP/JP]; 1-23-305, Goten, Hiratsuka-shi, Kanagawa-ken 254 (JP). SHIMIZU, Akio [JP/JP]; 103 Lumieru Takehi, 625-2, Shimo-Ochiai, Isenhara-shi, Kanagawa-ken 259-11 (JP). IKEDA, Toshihiro [JP/JP]; 3-33-13, Numame, Isenhara-shi, Kanagawa-ken 259-11 (JP).</p> <p>(74) Agent: FIGLIN, Cheryl, R.; Henkel Corporation, Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).</p>		<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, KE, KG, KP, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).</p> <p><b>Published</b>  <i>With international search report.  Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	

(54) Title: LOW SLUDGING COMPOSITION AND PROCESS FOR TREATING ALUMINUM AND ITS ALLOYS

(57) Abstract

A highly corrosion-resistant, strongly paint-adherent conversion coating is formed on the surface of aluminiferous metal substrates by contacting such surfaces for 0.5 to 60 seconds with a sludging-free water-based surface treatment bath that has a pH of 1.5 to 4.0 and contains a zirconium compound, phosphoric acid compound, oxidizing agent, and a compound that is a source of hydrogen fluoride (in a quantity that produces a concentration of from 0.0001 to 0.2 g/L HF in the treatment bath). This contact is preferably followed by a water rinse and drying.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Description**LOW SLUDGING COMPOSITION AND PROCESS FOR TREATING ALUMINUM AND ITS ALLOYS**Technical Field

This invention relates to a surface treatment composition and process that form a conversion coating on the surface of aluminiferous metals that imparts an excellent corrosion resistance and paint adherence to such surfaces prior to their painting. The aqueous solutions of this composition are transparent solutions that resist the production of a precipitating solid even when they contain eluted aluminum. The present invention is applied with particularly good effect to the surface treatment of drawn-and-ironed aluminum cans (hereinafter usually abbreviated as "aluminum DI cans"). Sludge adhesion to the equipment is inhibited and an excellent corrosion resistance and paint adherence are imparted to the substrate surface when aluminum DI cans fabricated by the drawing and ironing of aluminum alloy sheets are subjected, prior to their being painted and/or printed, to surface treatment with a surface treatment bath according to the present invention.

Background Art

The outside bottom surface of aluminum DI cans is subjected to high-temperature sterilization without being painted. If this region has a low corrosion resistance, the aluminum is oxidized and blackened during this step, and its appearance is thereby impaired. This phenomenon is generally known as "blackening". As a result, the (unpainted) conversion coating produced by surface treatment desirably should have an intrinsically high corrosion resistance.

At the present time, the surface treatment of aluminum DI cans is carried out mainly using Cr(VI)-containing phosphoric acid-chromate treatments and zirconium-type nonchromate treatments. These treatments are applied to the surfaces of the cans as aqueous liquid compositions, which hereinafter are usually called "baths" for brevity, even though they are more often applied by spraying the "bath" liquid onto cans than by immersion of the cans in the baths.

A typical example of nonchromate surface treatment baths is disclosed in

Japanese Patent Publication Number Sho 56-33468 [33,468/1981]. This surface treatment bath is an acidic (pH 1.5 to 4.0) water-based coating solution that contains phosphate, fluoride, and zirconium or titanium or a mixture thereof.

The characteristic features of this acidic nonchromate treatment bath are that it contains effective fluoride and does not contain a solid-producing component that is prone to precipitation. Since this nonchromate treatment bath does not contain toxic hexavalent chromium, it has come to be widely used at the present time as a surface treatment agent for aluminum DI cans. However, this bath in actuality also suffers from major drawbacks as described in the following.

When the prior art surface treatment baths are used on can manufacturing lines, they are ordinarily sprayed on the aluminum DI cans for about 15 to 30 seconds. When an object shaped like aluminum DI cans is subjected to spray treatment for such a brief period of time, the resulting coating may not be uniform, because of differences that occur between different regions of the can in the bath flow rate and in the contact conditions between the bath and the surface of the substrate. This creates variations or instabilities in the anticorrosion performance.

If, however, the production of a large conversion coating weight on the outside bottom surface of the can is pursued in order to stabilize the anticorrosion performance, too much conversion coating will be produced on the necking or flange regions that are processed after painting. This causes the problem of paint delamination after painting.

This variation in coating weight among the aforementioned regions is even more substantial in the case of aged surface treatment baths where the accumulated concentration of eluted aluminum in the solution has reached high values.

When the aforementioned prior art surface treatment bath is used industrially, avoiding unacceptable paint delamination results in the major drawback of requiring the use of an effective fluoride concentration, which essentially must be maintained at a constant value during use of the bath, that is somewhat smaller than that which would be most desirable for avoiding blackening and avoiding the formation of precipitates.

Due to this, when aluminum ions actually do elute and enter the bath, precipitation occurs even for the above-described surface treatment bath with its distinguishing feature of not containing a highly precipitation-prone solid-producing component. Even with this bath, then, problems such as equipment soiling, nozzle clogging, and the like, do in fact occur.

**Disclosure of the Invention**

**Problems to Be Solved by the Invention**

The present invention seeks to solve the problems described above for the prior art. In specific terms, the present invention introduces a bath and a process using said bath that not only are able to produce a highly corrosion-resistant, strongly paint-adherent conversion coating on the surfaces of aluminiferous metal substrates, but which also exhibit excellent properties in terms of conversion coating uniformity, sludging inhibition, and process stability.

**Summary of the Invention**

It has been discovered that:

- (i) a treatment bath that maintains a transparent appearance can be obtained when an oxidizing agent and a hydrogen fluoride-generating compound that produces a particular value for the HF concentration are also present in a surface treatment bath that contains a phosphoric acid compound and zirconium compound and has a pH of 1.5 to 4.0;
- (ii) an excellent corrosion resistance and good paint adherence can be imparted to the surface of aluminiferous metal substrates by the formation thereon of a conversion coating by contacting the surface of the aluminiferous metal with the aforesaid conversion bath for 0.5 to 60 seconds; and
- (iii) the conversion coating thereby formed is very uniform, while at the same time an excellent sludging inhibition is obtained.

The highly sludging-inhibited composition according to the present invention for treating the surface of aluminiferous metals is a waterborne surface treatment bath that forms a conversion coating on the surface of aluminiferous metals and is characterized in that it has a pH of 1.5 to 4.0 and comprises, preferably consists essentially of, or more preferably consists of water and the following components:

**THIS PAGE BLANK (USPTO)**

**THIS PAGE BLANK (USPTO)**

- (A) at least one phosphoric acid compound,  
(B) at least one zirconium compound,  
(C) at least one oxidizing agent, and  
(D) at least one compound that is a source of hydrogen fluoride, in a quantity that produces a total concentration of hydrogen fluoride in the aqueous solution in the range from 0.0001 to 0.2 grams per liter (hereinafter usually abbreviated as "g/L").

Detailed Description of the Invention and Preferred Embodiments Thereof

The aforesaid hydrogen fluoride-generating compound in the surface treatment composition according to the present invention is preferably selected from hydrofluoric acid and ammonium fluoride.

The aforesaid oxidizing agent in the surface treatment composition according to the present invention preferably consists of at least one selection from hydrogen peroxide, nitrous acid, organoperoxides, and salts of the preceding.

The aforesaid zirconium compound(s) are preferably present in a surface treatment composition according to the present invention at a total concentration of 0.005 to 0.5 g/L as zirconium.

The aforesaid phosphoric acid compound(s) is preferably present in a surface treatment composition according to the present invention at a concentration of 0.005 to 0.4 g/L as  $\text{PO}_4^{3-}$  ions. The total stoichiometric equivalent as  $\text{PO}_4^{3-}$  ions of all orthophosphoric acid (i.e.,  $\text{H}_3\text{PO}_4$ ), metaphosphoric acids (i.e.,  $[\text{HPO}_3]_x$ , where x is a positive integer with a value of at least 3), and condensed phosphoric acids (i.e.,  $\text{H}_{(n+2)}\text{P}_n\text{O}_{(3n+1)}$ , where n is a positive integer with a value of at least 2) and any anionic products formed by dissociation of any of these acids, including such anions added to the composition in the form of salts, is to be understood as constituting the  $\text{PO}_4^{3-}$  ions content for the definition of this concentration, irrespective of the actual extent of ionization, dissociation, and/or association that may occur in the surface treatment composition.

The aforesaid oxidizing agent is preferably present in the surface treatment composition according to the present invention at a concentration of 0.01 to 5.0 g/L.

A highly sludging-inhibited process according to the present invention for

treating the surface of aluminiferous metal substrates is characterized by the formation of a conversion coating on the surface of aluminiferous metal by contacting said surface for 0.5 to 60 seconds with a treatment bath containing any surface treatment composition as described directly above and thereafter, 5 optionally, subjecting said surface to a water rinse and drying.

When prior art surface treatment agents with their relatively slow reaction rates are sprayed on an article shaped like aluminum DI cans, the resulting conversion coating usually will not be uniform, because of differences in bath flow rate and surface/bath contact conditions that occur between different regions. The conversion coating may therefore exhibit an uneven performance. 10 In the specific case of aged surface treatment solutions in which the aluminum ions concentration in the solution has reached high levels, fluorine is consumed from the fluorocomplex of zirconium and it becomes necessary to add additional fluorine source in order to keep the zirconium stably dissolved in the bath, i.e., to keep the treatment bath transparent. This causes an even more pronounced 15 variation in coating weight among the various regions of the can.

The inventors discovered that the rate of the conversion coating formation reactions and the uniformity of the conversion coating can be improved through the presence of HF — in addition to zirconium, phosphoric acid, and oxidizing 20 agent — for the purpose of stabilizing the quality by eliminating the variations in coating weight between the regions of such a shaped article that would otherwise arise from differences in reaction rate.

It was also discovered that managing the HF concentration to 0.0001 to 25 0.2 g/L in order to inhibit precipitation of the zirconium in the treatment bath leads to an improved inhibition of sludge formation even in the case of aged treatment baths having high aluminum ion concentrations.

Coating formation is believed to occur during treatment with a zirconium-containing treatment bath because of an increase in pH at the interface between the metal substrate and the treatment bath. On the other hand, with regard to the hydrofluoric acid and aluminum fluorocomplexes present in conversion 30 treatment baths, it is known that the structures of these compounds change as a function of the pH of the treatment bath. Free fluoride (F), hydrofluoric acid

(HF), and various aluminum fluorocomplexes may be present in an acidic aqueous solution containing aluminum and fluorine. Their proportions vary with variations in the pH of the aqueous solution. Conversion coating formation reactions are believed to occur due to the decline in the HF concentration in the vicinity of the interface. Therefore, control of the HF concentration in the treatment bath becomes necessary in order to maintain a high conversion activity and a transparent appearance on the part of the treatment bath.

The HF concentration is measured in the present invention as follows. A commercially available fluoride ion reference solution is first diluted with a commercially available solution for adjusting the pH/ionic strength, in order to prepare three reference solutions with the following F<sup>-</sup> concentrations: F<sup>-</sup> = 1 mg/L, F<sup>-</sup> = 10 mg/L, and F<sup>-</sup> = 100 mg/L. These are then equilibrated at the specified temperature and used to calibrate the measurement values of a fluoride ion meter. A sample of the surface treatment solution is then equilibrated at the specified temperature, and its F<sup>-</sup> concentration is obtained using the calibrated fluoride ion meter and converted to the molar concentration, designated as "[F<sup>-</sup>]". The pH of the treatment bath is also measured and the molar H<sup>+</sup> concentration, designated as "[H<sup>+</sup>]", is derived from this. The molar concentration of HF, designated as "[HF]", is then calculated from the known dissociation constant for HF according to the following equation: [HF] = {[H<sup>+</sup>]•[F<sup>-</sup>]/10<sup>-3.17</sup>}. The [HF] value thus obtained is converted to g/L by multiplying by the gram molecular weight of HF.

The following concentrations are preferred for the surface treatment composition according to the present invention: for the zirconium compound, 0.005 to 0.5 g/L as zirconium; for the phosphoric acid compound, 0.005 to 0.4 g/L as PO<sub>4</sub> ions; for the oxidizing agent, 0.01 to 5 g/L.

With regard to the concentrations of the phosphoric acid compound, zirconium compound, and oxidizing agent in the surface treatment composition according to the present invention, if any of these falls below the above-specified lower limits, the resulting treatment bath will have an inadequate conversion coating formation activity and may not be able to lay down a conversion coating of sufficient thickness. No additional increases in effect are obtained when these

concentrations exceed the above-specified upper limits, and such concentrations therefore serve merely to raise the cost.

Zirconium-containing sludge is readily produced when the concentration of the hydrogen fluoride-source compound in the surface treatment composition according to the present invention falls below 0.0001 g/L as HF (hydrogen fluoride). An excessive etch, which impedes the formation of a conversion coating, occurs when this value exceeds 0.2 g/L.

A surface treatment process according to the present invention comprises the formation of a conversion coating by bringing the target surface of the aluminiferous metal substrate into contact with a treatment bath containing treatment composition as described above and then, optionally but preferably, executing thereon a water rinse and drying. Said contact between the treatment bath and metal surface may be implemented, using spray or immersion technology, as a continuous one-step process or as an intermittent multi-step process. The total contact time preferably should be from 0.5 to 60 seconds. Because the specific component composition of the treatment bath is able to inhibit sludge adhesion to the equipment, the described process according to the present invention can achieve an excellent operating stability and a high treatment efficiency.

The surface treatment bath according to the present invention is an acidic treatment bath that contains phosphate ions, a zirconium compound, fluoride, and oxidizing agent as its essential components. The source of the phosphate ions in this treatment bath preferably is phosphoric acid, ammonium phosphate, and/or an alkali metal salt of phosphoric acid, with phosphoric acid and ammonium phosphate more preferred, taking into consideration sludging inhibition. The content is preferably 0.005 to 0.4 g/L as phosphate ( $\text{PO}_4$ ) ions, while the range of 0.01 to 0.20 g/L as phosphate ion is even more preferred. Phosphate ion concentrations below 0.005 g/L result in a poor reactivity, which makes it very difficult to form satisfactory coatings. At the other extreme, no additional benefits are obtained at concentrations in excess of 0.4 g/L, which therefore serve merely to raise the cost of the treatment bath and thus are economically undesirable.

The presence of a zirconium compound in treatment baths according to the present invention is most advantageously brought about through the use of water-soluble compounds of zirconium, more preferably water-soluble fluorozirconium complexes and still more preferably fluozirconic acid ( $H_2ZrF_6$ ) and its salts. With regard to the use of the oxide, hydroxide, nitrate, or phosphate of zirconium, this should be accompanied by the simultaneous addition of fluoride that furnishes hydrogen fluoride in sufficient quantity to transform the zirconium into a water-soluble fluorocomplex and thereby prevent production of a precipitate. The zirconium compound content is preferably 0.005 to 0.5 g/L as zirconium and is more preferably 0.01 to 0.1 g/L as zirconium. Adequate film formation may not occur at a zirconium content below 0.005 g/L. No additional benefits are obtained at concentrations in excess of 0.5 g/L, which therefore serve merely to raise the cost of the treatment bath and thus are economically undesirable.

The presence of hydrogen fluoride in the treatment bath according to the present invention is most advantageously brought about by adding hydrofluoric acid or ammonium fluoride. The preferred HF content falls in the range of 0.0001 to 0.2 g/L and more preferably falls in the range of 0.01 to 0.1 g/L.

The oxidizing agent present in the treatment bath according to the present invention is exemplified by hydrogen peroxide, nitrous acid and its salts, and organoperoxides. The use of hydrogen peroxide is most preferred, based on a consideration of the ease of treating the waste water produced by the process according to the present invention. The oxidizing agent functions to accelerate the rate of the reactions that produce the zirconium coating. The oxidizing agent content is preferably 0.01 to 5 g/L and more preferably 0.1 to 1.0 g/L. The reaction-accelerating activity may be unsatisfactory at oxidizing agent concentrations below 0.01 g/L. No problems are associated with concentrations in excess of 5 g/L, but such concentrations do not provide any additional benefit, and thus merely drive up the costs and are therefore economically undesirable.

The pH of the treatment bath should be adjusted to 1.5 to 4.0. The extent of etching becomes excessive at pH values below 1.5 and impedes conversion coating formation. The etch becomes too weak at pH values in excess of 4.0 and makes it difficult to form a highly corrosion-resistant coating. The preferred

pH range is 2.3 to 3.0. The pH can be adjusted through the use of an acid such as phosphoric acid, nitric acid, or hydrochloric acid, or through the use of an alkali such as ammonium hydroxide, ammonium carbonate, or sodium hydroxide. Phosphoric acid and nitric acid are the preferred acids for adjusting the pH, while basic ammonium compounds are preferred as the alkali.

The stability of the treatment bath can be substantially impaired by metal ions, such as those of copper, manganese, and the like, that are produced when an alloying component is eluted from the surface of the aluminiferous metal substrate. This can result in such problems as sludge production, precipitate formation, and the adhesion of sludge and/or precipitate to the equipment and the like. In order to prevent this from happening, an organic acid or salt thereof, for example, gluconic acid, oxalic acid, and their salts, may be added in order to chelate such components and stabilize the bath.

A water-soluble fluorocomplex of, for example, titanium, silicon, and the like, may also be added to the surface treatment bath according to the present invention along with the zirconium compound, for example, a water-soluble fluorozirconium complex.

An example of the surface treatment process according to the present invention for an aluminiferous metal substrate includes the following steps:

- (1) surface cleaning: degreasing (acidic, alkaline, or solvent-based degreasers may be used)
- (2) water rinse
- (3) conversion coating treatment (surface treatment using a treatment bath according to the present invention)
- (4) water rinse
- (5) rinse with deionized water
- (6) drying

The treatment temperature with the surface treatment bath according to the present invention is not crucial, and, for example, a temperature range from room temperature to 90 °C can be used. However, taking into consideration the stability, operating behavior, and productivity characteristics of the treatment bath, the bath is preferably used at from 25 °C to 50 °C. The treatment time is

also not crucial, but treatment times of, for example, 0.5 to 60 seconds are preferred and the range of 5 to 30 seconds is even more preferred. A full reaction is not usually obtained in less than 5 seconds; this would prevent the formation of a highly corrosion-resistant coating. At the other end of the range, no additional increase in performance has been observed at times above 60 seconds.

The surface treatment bath and process according to the present invention will be illustrated through the working examples provided below.

### Examples

10 The following samples and performance evaluation tests were used in the working and comparative examples.

(1) Samples

15 The materials were aluminum alloy (A3004) sheets and aluminum DI cans fabricated from this type of aluminum alloy sheet. These were each cleaned, prior to surface treatment according to this invention, with a hot aqueous solution of an acidic degreaser (PALKLIN™ 500, a product of Nihon Parkerizing Company, Limited, Tokyo).

(2) Evaluation methods

(a) Corrosion resistance and coating uniformity

20 The corrosion resistance and coating uniformity were evaluated on the aluminum DI cans based on the resistance to blackening by boiling water. The resistance to blackening by boiling water was tested as follows. After surface treatment, the aluminum DI cans were immersed in boiling tap water for 30 minutes. This was followed by a visual determination of the degree of discoloration (blackening) thereby produced at the elevations (regions where the bath flow rate was fast) and depression (region where the bath flow rate was slow) of the aluminum DI cans. Said elevations correspond to the rib and exterior sidewall regions of actual aluminum DI cans, while the depression corresponds to the dome region.

25 The corrosion resistance was evaluated by scoring the test results on the following scale:

+ = no blackening

@ = blackening over part of the surface  
x = blackening over the entire surface.

The coating uniformity was rated as follows based on the resulting location-specific evaluation of the resistance to blackening by boiling water: a score of "uniform" was rendered when both locations were free of blackening, while a score of "nonuniform" was rendered when blackening occurred at only one location.

5 (b) Paint adherence

10 After the aluminum alloy (A3004) sheet had been subjected to the surface treatment, it was coated with a can-grade epoxy-urea paint to give a paint film thickness of 5 to 7 micrometers. This was followed by baking and drying to give a painted panel. A test panel was then prepared by bending the painted panel in a bending tester, and this test panel was subjected to a peel test using cellophane tape. The test results were scored as follows:

15 + = peeling did not occur  
x = peeling occurred.

(c) Bath transparency

20 The treatment bath which had been used in the particular example or comparative example was held at 40 °C for 15 days. The amount of zirconium in the bath was measured both before and after this holding period, and the presence/absence of precipitate was determined from the difference in these values. A "+" indicates that precipitate was not produced, while "X" indicates that precipitate was produced.

(d) Confirming test for sludge adhesion

25 The treatment bath which had been used in the particular example or comparative example was supplied continuously for 16 hours to spray treatment using a small-scale sprayer held at 40 °C. During this time, the development of sludge at the nozzle of the device was inspected visually. A "+" indicates no sludge adhesion, while "x" indicates that sludge adhesion occurred.

30 Example 1

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were sprayed for 20 seconds with surface treatment bath (1) (composition given

below) heated to 40 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying oven. The samples thus obtained were evaluated for their corrosion resistance, coating uniformity, and paint adherence.

5 The aluminum nitrate was used as an aluminum source for the purpose of artificially aging the treatment bath.

#### Surface treatment bath (1)

phosphoric acid	30 ppm as PO <sub>4</sub> ions
fluozirconic acid	30 ppm as Zr
10 hydrogen peroxide	100 ppm as H <sub>2</sub> O <sub>2</sub>
aluminum nitrate	100 ppm as Al

pH = 3.0 (adjusted with aqueous ammonia)

concentration of HF = 11 ppm (adjusted with hydrofluoric acid).

#### Example 2

15 The cleaned aluminum DI cans and cleaned aluminum alloy sheets were sprayed for 40 seconds with surface treatment bath (2) (composition given below) heated to 40 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying oven. The samples thus obtained were evaluated for their corrosion resistance, coating 20 uniformity, and paint adherence.

#### Surface treatment bath (2)

phosphoric acid	20 ppm as PO <sub>4</sub> ions
fluozirconic acid	10 ppm as Zr
hydrogen peroxide	300 ppm as H <sub>2</sub> O <sub>2</sub>
25 aluminum nitrate	50 ppm as Al

pH = 2.7 (adjusted with aqueous ammonia)

concentration of HF = 9 ppm (adjusted with hydrofluoric acid)

#### Example 3

30 The cleaned aluminum DI cans and cleaned aluminum alloy sheets were sprayed for 15 seconds with surface treatment bath (3) (composition given below) heated to 40 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying

oven. The samples thus obtained were evaluated for their corrosion resistance, coating uniformity, and paint adherence.

Surface treatment bath (3)

phosphoric acid	40 ppm as PO <sub>4</sub> ions
fluozirconic acid	40 ppm as Zr
hydrogen peroxide	200 ppm as H <sub>2</sub> O <sub>2</sub>
aluminum nitrate	200 ppm as Al
pH = 2.3 (adjusted with aqueous ammonia)	
concentration of HF = 15 ppm (adjusted with hydrofluoric acid)	

10

Example 4

15

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were immersed for 10 seconds in surface treatment bath (4) (composition given below) heated to 30 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying oven. The samples thus obtained were evaluated for their corrosion resistance, coating uniformity, and paint adherence.

Surface treatment bath (4)

phosphoric acid	150 ppm as PO <sub>4</sub> ions
fluozirconic acid	100 ppm as Zr
hydrogen peroxide	400 ppm as H <sub>2</sub> O <sub>2</sub>
aluminum nitrate	300 ppm as Al
pH = 2.5 (adjusted with aqueous ammonia)	
concentration of HF = 70 ppm (adjusted with hydrofluoric acid)	

Example 5

25

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were sprayed for 5 seconds with surface treatment bath (5) (composition given below) heated to 30 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying oven. The samples thus obtained were evaluated for their corrosion resistance, coating uniformity, and paint adherence.

30

Surface treatment bath (5)

phosphoric acid	400 ppm as PO <sub>4</sub> ions
ammonium fluozirconate	200 ppm as Zr
hydrogen peroxide	500 ppm as H <sub>2</sub> O <sub>2</sub>
aluminum nitrate	500 ppm as Al

5 pH = 2.5 (adjusted with aqueous ammonia)

concentration of HF = 100 ppm (adjusted with hydrofluoric acid).

Example 6

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were  
10 sprayed for 15 seconds with surface treatment bath (6) (composition given  
below) heated to 40 °C. This was followed by rinsing with tap water, spray rins-  
ing for 10 seconds with deionized water, and then drying in a hot-air drying oven.  
The samples thus obtained were evaluated for their corrosion resistance, coating  
uniformity, and paint adherence.

Surface treatment bath (6)

phosphoric acid	50 ppm as PO <sub>4</sub> ions
zirconium oxide	30 ppm as Zr
hydrogen peroxide	200 ppm as H <sub>2</sub> O <sub>2</sub>
aluminum nitrate	200 ppm as Al

20 pH = 2.3 (adjusted with aqueous ammonia)

concentration of HF = 13 ppm (adjusted with hydrofluoric acid)

Example 7

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were  
sprayed for 15 seconds with surface treatment bath (7) (composition given  
25 below) heated to 40 °C. This was followed by rinsing with tap water, spray rins-  
ing for 10 seconds with deionized water, and then drying in a hot-air drying oven.  
The samples thus obtained were evaluated for their corrosion resistance, coating  
uniformity, and paint adherence.

Surface treatment bath (7)

phosphoric acid	50 ppm as PO <sub>4</sub> ions
zirconium oxide	30 ppm as Zr
hydrogen peroxide	200 ppm as H <sub>2</sub> O <sub>2</sub>

aluminum nitrate                                    100 ppm as Al

pH = 3.5 (adjusted with aqueous ammonia)

concentration of HF = 7 ppm (adjusted with hydrofluoric acid).

Comparative Example 1

5         The cleaned aluminum DI cans and cleaned aluminum alloy sheets were sprayed for 10 seconds with surface treatment bath (8) (composition given below) heated to 40 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying oven. The samples thus obtained were evaluated for their corrosion resistance, 10 coating uniformity, and paint adherence.

Surface treatment bath (8) (no oxidizing agent)

phosphoric acid	30 ppm as PO <sub>4</sub> ions
fluozirconic acid	30 ppm as Zr
aluminum nitrate	200 ppm as Al

15         pH = 3.0 (adjusted with aqueous ammonia)

concentration of HF = 15 ppm (adjusted with hydrofluoric acid).

Comparative Example 2

20         The cleaned aluminum DI cans and cleaned aluminum alloy sheets were sprayed for 10 seconds with surface treatment bath (9) (composition given below) heated to 50 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying oven. The samples thus obtained were evaluated for their corrosion resistance, coating 25 uniformity, and paint adherence.

Surface treatment bath (9) (no zirconium compound)

25         phosphoric acid	50 ppm as PO <sub>4</sub> ions
hydrofluoric acid	220 ppm as F
hydrogen peroxide	500 ppm as H <sub>2</sub> O <sub>2</sub>
aluminum nitrate	100 ppm as Al

pH = 2.5 (adjusted with aqueous ammonia)

30         concentration of HF = 10 ppm (adjusted with hydrofluoric acid)

Comparative Example 3

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were

sprayed for 20 seconds with surface treatment bath (10) (composition given below) heated to 35 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying oven. The samples thus obtained were evaluated for their corrosion resistance, coating uniformity, and paint adherence.

Surface treatment bath (10)

fluozirconic acid	40 ppm as Zr
hydrogen peroxide	500 ppm as H <sub>2</sub> O <sub>2</sub>
aluminum nitrate	200 ppm as Al
10 pH = 3.0 (adjusted with aqueous ammonia)	
concentration of HF = 50 ppm (adjusted with hydrofluoric acid).	

Comparative Example 4

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were sprayed for 15 seconds with surface treatment bath (11) (composition given below) heated to 40 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying oven. The samples thus obtained were evaluated for their corrosion resistance, coating uniformity, and paint adherence.

Surface treatment bath (11)

20 phosphoric acid	50 ppm as PO <sub>4</sub> ions
fluozirconic acid	50 ppm as Zr
hydrogen peroxide	300 ppm as H <sub>2</sub> O <sub>2</sub>
aluminum nitrate	200 ppm as Al
25 pH = 2.7 (adjusted with aqueous ammonia)	
concneteration of HF = 0.05 ppm (adjusted with hydrofluoric acid).	

Comparative Example 5

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were sprayed for 10 seconds with surface treatment bath (12) (composition given below) heated to 40 °C. This was followed by rinsing with tap water, spray rinsing for 10 seconds with deionized water, and then drying in a hot-air drying oven. The samples thus obtained were evaluated for their corrosion resistance, coating uniformity, and paint adherence.

Surface treatment bath (12)

phosphoric acid	40 ppm as PO <sub>4</sub> ions
zirconium oxide	40 ppm as Zr
hydrogen peroxide	300 ppm as H <sub>2</sub> O <sub>2</sub>
aluminum nitrate	200 ppm as Al
pH = 2.8 (adjusted with aqueous ammonia)	
concentration of HF = 0.01 ppm (adjusted with hydrofluoric acid).	

Comparative Example 6

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were  
 10 sprayed for 15 seconds with surface treatment bath (13) (composition given  
 below) heated to 40 °C. This was followed by rinsing with tap water, spray  
 rinsing for 10 seconds with deionized water, and then drying in a hot-air drying  
 oven. The samples thus obtained were evaluated for their corrosion resistance,  
 coating uniformity, and paint adherence.

Surface treatment bath (13)

phosphoric acid	40 ppm as PO <sub>4</sub> ions
fluozirconic acid	40 ppm as Zr
aluminum nitrate	300 ppm as Al
pH = 3.0 (adjusted with aqueous ammonia)	
concentration of HF = 15 ppm (adjusted with hydrofluoric acid).	

Comparative Example 7

The cleaned aluminum DI cans and cleaned aluminum alloy sheets were  
 20 sprayed for 30 seconds with surface treatment bath (14) (composition given  
 below) heated to 40 °C. This was followed by rinsing with tap water, spray rins-  
 ing for 10 seconds with deionized water, and then drying in a hot-air drying oven.  
 The samples thus obtained were evaluated for their corrosion resistance, coating  
 uniformity, and paint adherence.

Surface treatment bath (14)

phosphoric acid	100 ppm as PO <sub>4</sub> ions
fluozirconic acid	100 ppm as Zr
aluminum nitrate	300 ppm as Al
pH = 3.0 (adjusted with aqueous ammonia)	

concentration of HF = 20 ppm (adjusted with hydrofluoric acid).

Test results from all the Examples and Comparative examples are reported in Table 1.

Examples 1 to 7 used surface treatment baths and surface treatment processes according to the present invention, and Table 1 confirms the following results for these examples: the obtained conversion coatings exhibited an excellent corrosion resistance and paint adherence; the obtained conversion coatings were very uniform; the surface treatment baths maintained their transparency; and sludge adhesion was thoroughly inhibited. In contrast, Comparative Examples 1 to 7 — which used surface treatment baths outside the scope of the invention — in each case gave an unsatisfactory overall performance because each was found to be deficient in at least one aspect (corrosion resistance, paint adherence, conversion coating uniformity, treatment bath transparency, and inhibition of sludge adhesion).

The surface treatment composition and surface treatment process according to the present invention impart an excellent corrosion resistance and excellent paint adherence to the surface of aluminiferous metal substrates prior to the painting thereof. Other desirable effects demonstrated by this composition and process are a very uniform conversion coating, excellent treatment bath transparency, and an excellent inhibition of sludge adhesion.

These characteristics confer a high degree of practical utility on the bath and process according to the present invention for treating the surface of aluminiferous metal substrates.

TABLE 1

Example or Comparison Example	Corrosion Resistance and Uniformity			Paint Adherence	Bath Transparency	Inhibition of Sludge Adhesion
	Elevations	Depressions	Uniformity			
Ex 1	+	+	uniform	+	+	+
Ex 2	+	+	uniform	+	+	+
Ex 3	+	+	uniform	+	+	+
Ex 4	+	+	uniform	+	+	+
Ex 5	+	+	uniform	+	+	+
Ex 6	+	+	uniform	+	+	+
Ex 7	+	+	uniform	+	+	+
CE 1	x	x	-	+	+	+
CE 2	x	x	-	+	+	+
CE 3	x	x	-	+	+	+
CE 4	+	+	uniform	+	x	x
CE 5	x	@	nonuniform	+	x	x
CE 6	x	+	nonuniform	+	+	+
CE 7	@	+	nonuniform	x	+	+

Abbreviations for Table 1

"Ex" = "Example"; "CE" = "Comparative Example".

Claims

1. A highly sludging-inhibited aqueous liquid composition for treating the surface of aluminiferous metals, said composition having a pH of 1.5 to 4.0 and comprising water and:
  - (A) at least one phosphoric acid compound,
  - (B) at least one zirconium compound,
  - (C) at least one oxidizing agent, and
  - (D) at least one compound that is a source of hydrogen fluoride, in a quantity that produces a total concentration of hydrogen fluoride in the aqueous composition in the range from 0.0001 to 0.2 g/L.
2. An aqueous liquid composition according to claim 1, in which component (D) is selected from the group consisting of hydrofluoric acid, ammonium fluoride, and mixtures thereof.
3. An aqueous liquid composition according to claim 2, in which component (C) is selected from the group consisting of hydrogen peroxide, nitrous acid and its salts, organoperoxides, and mixtures of any two or more of the preceding.
4. An aqueous liquid composition according to claim 1, in which component (C) is selected from the group consisting of hydrogen peroxide, nitrous acid and its salts, organoperoxides, and mixtures of any two or more of the preceding.
5. An aqueous liquid composition according to claim 4, in which the concentration of component (B) is from 0.005 to 0.5 g/L, measured as zirconium.
6. An aqueous liquid composition according to claim 3, in which the concentration of component (B) is from 0.005 to 0.5 g/L, measured as zirconium.
7. An aqueous liquid composition according to claim 2, in which the concentration of component (B) is from 0.005 to 0.5 g/L, measured as zirconium.
8. An aqueous liquid composition according to claim 1, in which the concentration of component (B) is from 0.005 to 0.5 g/L, measured as zirconium.
9. An aqueous liquid composition according to claim 8, in which the concentration of component (A) is from 0.005 to 0.4 g/L as  $\text{PO}_4$  ions.

10. An aqueous liquid composition according to claim 7, in which the concentration of component (A) is from 0.005 to 0.4 g/L as PO<sub>4</sub> ions.
11. An aqueous liquid composition according to claim 6, in which the concentration of component (A) is from 0.005 to 0.4 g/L as PO<sub>4</sub> ions.
12. An aqueous liquid composition according to claim 5, in which the concentration of component (A) is from 0.005 to 0.4 g/L as PO<sub>4</sub> ions.
13. An aqueous liquid composition according to claim 4, in which the concentration of component (A) is from 0.005 to 0.4 g/L as PO<sub>4</sub> ions.
14. An aqueous liquid composition according to claim 3, in which the concentration of component (A) is from 0.005 to 0.4 g/L as PO<sub>4</sub> ions.
15. An aqueous liquid composition according to claim 2, in which the concentration of component (A) is from 0.005 to 0.4 g/L as PO<sub>4</sub> ions.
16. An aqueous liquid composition according to claim 1, in which the concentration of component (A) is from 0.005 to 0.4 g/L as PO<sub>4</sub> ions.
17. An aqueous liquid composition according to any one of claims 1 through 16, in which the concentration of component (C) is 0.01 to 5.0 g/L.
18. A process of forming a protective conversion coating on an aluminiferous substrate surface, said process comprising contacting the substrate surface with an aqueous liquid composition according to claim 17 for from 0.5 to 60 seconds, and, optionally, thereafter subjecting said substrate surface to a water rinse and drying.
19. A process of forming a protective conversion coating on an aluminiferous substrate surface, said process comprising contacting the substrate surface with an aqueous liquid composition according to any one of claims 1 through 16 for from 0.5 to 60 seconds, and, optionally, thereafter subjecting said substrate surface to a water rinse and drying.

## INTERNATIONAL SEARCH REPORT

INTERNATIONAL APPLICATION NO.

PCT/US95/16231

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) C23C 22/10

US CL 148/247

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/247

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,139,586 (DAS) 18 August 1992, col. 5, lines 5-40.	1-19
Y	US, A, 3,539,403 (RIES) 10 November 1970, col 2, lines 20-45.	1-19

 Further documents are listed in the continuation of Box C. See patent family annex.

Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance		"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date		"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means			
"P" document published prior to the international filing date but later than the priority date claimed			

Date of the actual completion of the international search

04 APRIL 1996

Date of mailing of the international search report

15 MAY 1996

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SAM SILVERBERG

Telephone No. (703) 305-9646